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Hysteresis-free electron currents in poly(*p*-phenylene vinylene) derivatives

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The interpretation of electron currents in conjugated polymers is strongly hindered by the occurrence of hysteresis. We investigate the transport of electrons in electron-only devices based on derivatives of poly(p-phenylene vinylene) (PPV) for various hole-blocking bottom electrodes as well as purification of the polymer. The use of a variety of hole blocking bottom contacts, as metallic electrodes and n-type doped polymers, did not give any improvement in the observed hysteresis. By purification of the PPV, hysteresis free electron-only currents can be obtained. The deep traps responsible for hysteresis, with a concentration in the 10^{16} cm^{-3} range, are not responsible for the trap-limited electron transport as observed in purified PPV. © *2010 American Institute of Physics*. [doi:10.1063/1.3432744]

I. INTRODUCTION

Charge transport is an important issue with regard to the understanding and optimization of electronic devices made from conjugated polymers. In the last two decades a large effort has been put on the characterization of the transport of holes, which is the dominant charge carrier. It has been demonstrated that the hole transport is governed by hopping between localized states,[1] characterized by a mobility that depends on density, electric field, and temperature.[2,3] At room temperature the dependence of the mobility on carrier density governs the hole conduction, whereas at low temperatures the field dependence dominates.[4] The transport of electrons is less well established, and the strongly reduced electron currents are attributed to trapping of electrons.[5] The strong dependence on applied voltage and sample thickness, as observed in poly(2-methoxy-5–3,7-dimethyloctyloxy-p-phenylene vinylene) (MDMO-PPV), was explained by the presence of traps with an exponential distribution of trapping sites in energy.[5] These traps have been attributed to impurities related to molecular oxygen.[6] A major problem with the investigation of the electron transport is the construction of so-called electron-only devices, where hole blocking electrodes are required that are usually reactive. The resulting current density versus voltage (*J-V*) characteristics of these devices often exhibit, next to low currents, strong hysteresis effects. Hysteresis effects often originate from the presence of deeply trapped charges of which the escape time is longer than the time it takes to make the *J-V* sweep. As a result after the first sweep the device is still charged and out of equilibrium, and a subsequent *J-V* sweep is influenced by the presence of these deeply trapped charges. This strongly hinders the interpretation of the electron currents, especially in cases where a series of subsequent sweeps are made as, for example, a temperature scan. In some cases, but not reproducibly, we were able to obtain nearly hysteresis free electron currents: the weak temperature of these trap-limited electron currents in MDMO-PPV and other PPV derivatives could then be explained by a trap model that incorporates the presence of a Gaussian density of states for free electrons.[7] However, the presence and origin of the hysteresis in most of the electron currents has not been addressed so far. Major candidates responsible for the strong hysteresis are electrons deeply trapped either in the bulk of the polymer or at the hole blocking electrode/polymer interface. We investigate the transport of electrons in electron-only devices based on MDMO-PPV and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) for a variety of hole-blocking bottom electrodes, as well as purification of the polymer. We demonstrate that after the purification step hysteresis free electron currents are obtained, showing that the hysteresis originates from electrons being trapped at an impurity in the polymer.

II. EXPERIMENTAL

A major experimental problem with the investigation of the electron transport is the construction of the electron-only devices, where hole blocking bottom electrodes are required that are usually reactive. During spincoating of the polymer such a reactive bottom electrode might react with the polymer solution. As a result next to deep traps in the polymer layer itself also electrons trapped at the hole blocking electrode/polymer interface might be a source of hysteresis. In order to discriminate between bulk trapping and interface trapping we fabricated electron-only devices on a variety of metallic bottom electrodes. Next to the standard Al electrode also bottom electrodes of Yb, Ga, and In were used. All the

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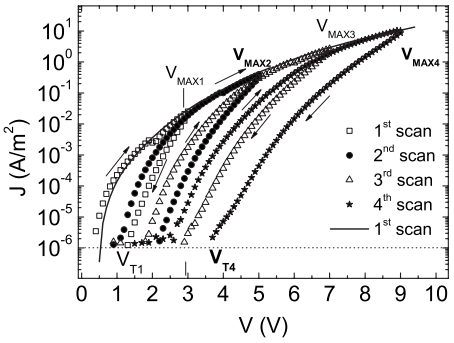

FIG. 1. Subsequent *J-V* characteristic of a Al/MEH-PPV/Ba/Al electron-only device with a thickness of 150 nm. With every sweep the maximum voltage is increased with 2 V. The solid line represents the up-scan of a *J-V* measurement for a fresh device of the same thickness $L=150$ nm.

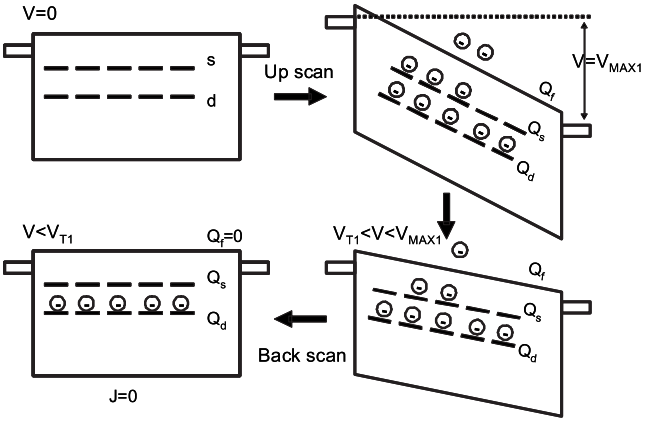

FIG. 2. Filling of shallow and deep traps during the up-scan of a *J-V* measurement. During the back-scan the deep traps are not emptied, leading to clockwise hysteresis.

electrodes were prepared by thermal evaporation at low pressure $10^{-7}-10^{-6}$ mbar, with a thickness of 20 nm on top of indium tin oxide coated glass. Subsequently either MDMO-PPV or MEH-PPV was spin coated from toluene solution. For the synthesis of the MEH-PPV 500 mg of Gilch MEH monomer was dissolved in dry dioxane (0.02 M). The mixture was stirred at 25 °C under a continuous flow of nitrogen. 2.6 equivalents of a KtBuO solution (0.87 M in dioxane) were added dropwise over a time period of 15 min to the stirred monomer solution. After a waiting period of 10 min another two equivalents of a KtBuO solution (0.90 M in dioxane) were added in one go. During the addition of base an insoluble gel is formed. The reaction proceeded for 2 h at 25 °C under a nitrogen atmosphere. Subsequently, the temperature was set at 100 °C and the mixture reacted for another 16 h under dark conditions to decrease the amount of gel. After reaction the mixture was cooled and subsequently precipitated in 500 ml stirred cold methanol. The mixture was filtered and the polymer was collected. The total yield of the reaction amounts to 50%. In order to finish the electron-only devices barium (Ba) top electrodes were vapor deposited and coated with a protective aluminum layer. Current density-voltage *J-V* measurements were performed in the dark and under a N_2 atmosphere, using a computer-controlled source meter unit Keithley 2400.

III. RESULTS AND DISCUSSION

In Fig. 1 subsequent *J-V* sweeps are shown for an Al/MEH-PPV/Ba/Al electron-only device. The thickness of the MEH-PPV amounts to 150 nm. In the first sweep the voltage is scanned from 0–3 V and back, in the second sweep from 0–5 V and back, and at every subsequent sweep the maximum applied voltage is increased with 2 V.

In the first sweep the up-scan shows an electron current that is typical for MEH-PPV, whereas the back-scan shows a strong decrease directly when going down from the maximum applied voltage on, and at a finite voltage V_{T1} (1.4 V) the electron current even decreases to values below the sensitivity of the set-up ($J=10^{-6}$ A/m^2 as indicated by the dashed line in Fig. 1, determined by the sensitivity of the source-measure unit). The up-scan of the second sweep then closely follows the back-scan of the first sweep; first there is no measurable current and from V_{T1} it strongly increases. For voltages higher than the maximum voltage V_{MAX1} of the first sweep (5 V), the up-scan connects to the up-scan of the first sweep. The back-scan of the second sweep then decreases again and becomes undetectable at a voltage V_{T2} (2.2 V). This behavior then repeats for every subsequent sweep. It should also be noted that when a fresh device is directly swept to a higher voltage of 9 V (Fig. 1, solid line), its up-scan forms the envelope of the up-scans of the other sweeps that were carried out with a lower maximum voltage. Identical results were also observed for electron-only devices based on MDMO-PPV.

This behavior can be explained as follows, schematically indicated in Fig. 2. We consider a semiconductor that is sandwiched between two Ohmic contacts. The semiconducting material contains both shallow (s) and deep (d) traps. At zero bias the fresh device is free of trapped charges [Fig. 2(a)]. On application of a voltage the device is charged with carriers from the contact, resulting in a trap-limited current. The total amount of carriers injected into the device at a given voltage V is approximately given by C_0V, with C_0 the geometrical capacitance. For a trap-free space-charge limited device the amount of charges equals exactly 1.5 C_0V, for a trap-limited device it is closer to C_0V since the traps confine the carriers closer to the injecting electrode.[8] Thus, at the maximum voltage V_{MAX1} the total amount of charges in the device typically amounts to C_0V_{MAX}. These charges can either be free (Q_f), trapped in shallow traps (Q_s) that are in thermal equilibrium with the free carriers, and trapped in deep traps (Q_d) from which they cannot escape [Fig. 2(b)]. On the back-scan, when the voltage is lowered also the amount of charges C_0V that is electrostatically allowed in the device will be lowered.

However, since Q_d cannot be removed, only Q_f and Q_s will be decreased [Fig. 2(c)], leading to a very strong reduction in the current during the back-scan. As a result clockwise hysteresis will occur. At the voltage V_{T1} given by $Q_d = C_0 \times V_{T1}$ the charges Q_f and Q_s will be completely removed from the sample and the current will go to zero [Fig. 2(d)], since the presence of free charges is electrostatically not allowed anymore. For lower voltages than V_{T1} (1.4 V) the current will remain zero, since Q_d exceeds C_0V and the system is completely out of equilibrium. For the second

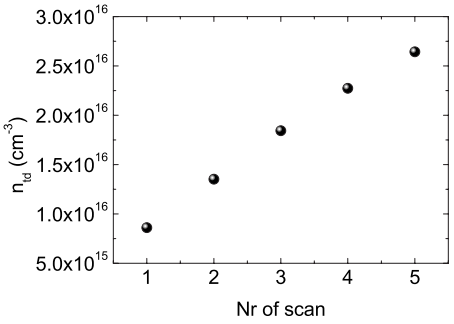

FIG. 3. Concentration of charges remaining in deep traps after subsequent *J-V* sweeps with increasing maximum applied voltage V_{MAX}.

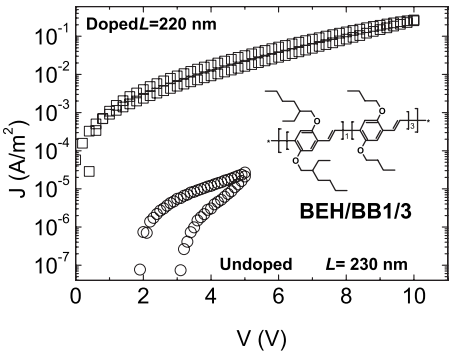

FIG. 5. *J-V* characteristics of both an undoped BEH-BB-PPV (1:3) electron-only (circles) and doped (squares) electron-only device.

sweep no current will flow until the applied voltage reaches V_{T1}. For $V > V_{T1}$ it is electrostatically allowed to inject free carriers again, leading to a strong increase in the current. For $V > V_{MAX1}$ it is even allowed to further fill-up the deep traps and also Q_d will further increase. In that case the up-scan will start to connect to the up-scan of the previous sweep. This process will continue for every subsequent sweep with a higher V_{MAX}. From the observed values of V_{T1}, V_{T2}, and so on, we can estimate the amount of deeply trapped electrons that stay behind in the device after each sweep. The total amount of charge carriers per area then increases from 1.4×10^{11} cm^{-2} after the first sweep to 4.2×10^{11} cm^{-2} after the fifth sweep. The average density of deeply trapped electrons per volume n_{td} is shown in Fig. 3, and increases from 8.6×10^{15} to 2.6×10^{16} cm^{-3} after five sweeps. It should be noted that this concentration is at least an order of magnitude lower than the values of 5×10^{17} cm^{-3} estimated for the (effective) total amount of electron traps that follow from the analysis of the (up-scan) *J-V* characteristics.[7]

An important question is now whether these deeply trapped electrons are located in the bulk of the polymer, as sketched in Fig. 1, or at the hole blocking bottom electrode. Figure 4 shows the *J-V* characteristics of MDMO-PPV based electron-only diodes made with Ga, In, and Yb bottom electrodes at room temperature. The fact that the measured currents are nearly independent of the choice of the bottom electrode confirms the absence of chemical interactions between the bottom electrodes and the polymer. For voltages larger than 10 V the devices with In and Ga show a slight enhancement of the current, that is accompanied by the onset of light-emission (not shown). This demonstrates that for these

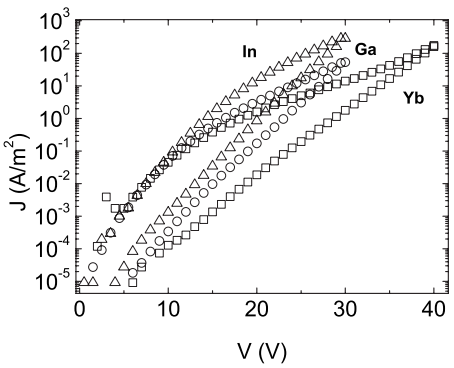

FIG. 4. *J-V* characteristics of electron-only diodes with different hole blocking bottom electrodes (Metal/MDMO-PPV/Ba/Al).

electrodes hole injection starts to occur, and the measured currents are not solely due to the electrons anymore. The most important observation is that there is no change in the hysteresis behavior. This indicates that trapped electrons at the bottom contact/polymer interface are not responsible for the observed hysteresis effects.

In a recent study we demonstrated that in MEH-PPV the trap-limited currents can be strongly increased by addition of the n-type dopant decamethylcobaltocene (DMC).[9] By filling the traps with electrons from the DMC donor a trap- and hysteresis-free space-charge limited electron current can be obtained in MEH-PPV. As a next step we use an n-type doped PPV-based polymer as an interlayer between the metallic bottom electrode and the undoped MEH-PPV layer polymer for the fabrication of double-layer electron-only devices. In this case the electron extracting electrode is not metallic, but a n-type doped polymer. However, in order to use such a n-type doped polymer layer as bottom electrode the layer should not dissolve when the undoped MEH-PPV layer is spincoated on top of it. A way to circumvent the solubility issue is to tune the solubility by chemical modification,[10] PPV-based copolymers with selective solubility can be achieved without loss of the charged transport properties. It was shown that by shortening the (2′-ethylhexyloxy) side chains, from poly[2,5-bis(2′-ethylhexyloxy)-1,4-phenylenevinylene] (BEH-PPV), to butoxy side chains the polymer poly[2,5-bis(butoxy)-1,4-phenylenevinylene] (BB-PPV) was obtained, which is only soluble in chloroform in very low concentrations. Consequently, by tuning the ratio of the BEH- and BB-monomers the solubility could be adjusted over the whole spectrum of solvents. For example, the BEH-BB-PPV copolymer in a 1:3 ratio was only soluble in chloroform, making it compatible with a large number of light-emitting polymers as MEH-PPV. In Fig. 5 the *J-V* characteristics of an undoped BEH-BB-PPV (1:3) and a DMC doped electron-only device is shown. The chemical structure of BEH-BB-PPV (1:3) is shown in the inset of Fig. 5. Similar as to earlier results on MEH-PPV the electron current increases a few orders of magnitude, accompanied with an (almost) disappearance of the hysteresis. This already demonstrates that the electrons from the dopants not only fill the trap states that are responsible for the low electron currents, but also the trap states that are responsible for the hysteresis.

The electron current of the double-layer device, with an

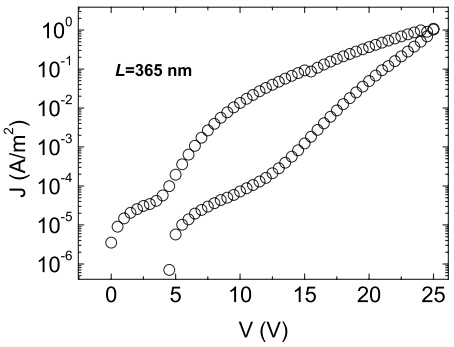

FIG. 6. *J-V* characteristics of an electron-only device measured for a double layer: doped BEH-BB1:3 and undoped MDMO-PPV.

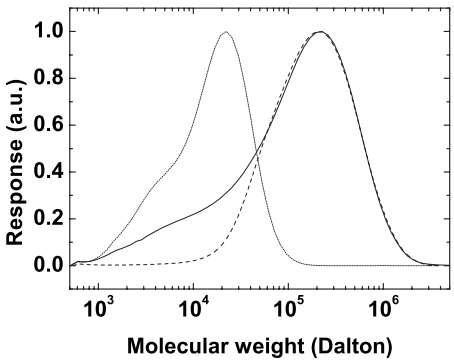

FIG. 7. Overlay of SEC chromatograms of unpurified MEH-PPV (solid line), high molecular weight MEH-PPV precipitate (dashed line), and low molecular weight MEH-PPV filtrate (dotted line).

undoped MDMO-PPV layer on top of the n-doped BEH-BB PPV layer is shown in Fig. 6. It appears that addition of the MDMO-PPV layer directly results in a large hysteresis. This clearly shows that the hysteresis originates from electron trapping in the bulk of the undoped MDMO-PPV.

In order to reduce or eliminate the hysteresis from the electron currents the deep traps have to be removed from the polymer material itself. In a recent study it has been demonstrated that the optoelectronic properties of poly(3-hexylthiophene) can be strongly modified by treating the polymer solution with either electrophiles or nucleophiles.[11] The p-type defects could be strongly reduced by a treatment with lithium aluminum hydride, whereas treatment with dimethylsulfate gives rise to a removal of anionic sites. For purification of our PPV derivatives we followed an alternative approach with the aim to decrease the polydispersity (PD). For this purpose a number of subsequent precipitations have been carried out. The precipitates were always filtered on a Whatman vacuum filtration unit, using hydrophobic polytetrafluoroethylene membrane filters with a pore size of 0.45 μm from PALL Life Sciences. The crude MEH-PPV was dissolved in $CHCl_3$ (5 mg/ml) at 60 °C overnight under nitrogen atmosphere. The solution was filtered to isolate the soluble polymer filtrate from the insoluble gel parts which stayed on the filter. A sample of the filtrate was subjected to analytical size exclusion chromatography (SEC), which was performed using a Spectra series P100 (Spectra Physics) pump equipped with two mixed-B columns (10 μm, 2 $\times 30$ cm^2, Polymer Laboratories) and a refractive index detector (Shodex) at 70 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. Molecular weight distributions are given relative to polystyrene standards. The results can be found in Table I. To decrease the PD of the polymer mixture, cold methanol was added dropwise to the filtrate until the polymer starts to precipitate. Via this reverse precipitation, the larger polymer chains precipitate first while the shorter ones stay in solution. This way, only the high molecular weight polymer can be isolated by filtering the mixture. As can be seen in Table I, PD has decreased from 11.9 till 3.2 in the polymer precipitate. The SEC chromatograms of the three samples are given in Fig. 7. The high molecular weight M_w polymer precipitate was purified further by two subsequent precipitations in, respectively, 500 ml acetone and 500 ml methanol. The final polymer precipitate was collected and dried in vacuum overnight. The polymer is stored in dark under a nitrogen atmosphere.

TABLE I. Purification results for MEH-PPV before and after reversed precipitation, determined by means of SEC in THF using polystyrene standards.

SEC sample	M_w	PD
Unpurified MEH-PPV	236 000	11.9
Reversed precipitation: precipitate (high M_w MEH-PPV)	296 000	3.2
Reversed precipitation: filtrate (low M_w MEH-PPV)	19 000	2.7

After this purification procedure electron-only devices were again fabricated. In Fig. 8 the up- and back-scan of the electron current for a purified MEH-PPV is shown for a thickness of 300 nm. We observe that after purification the hysteresis has completely disappeared. As a comparison also the *J-V* characteristics of unpurified MEH-PPV is shown, with a film thickness of 340 nm. Here the electron current is lower and shows a clear hysteresis. The *J-V* characteristics of the purified MEH-PPV show the usual steep voltage dependence and are modeled with a trap distribution that is exponentially distributed in energy. The parameters obtained are identical as the ones reported before.[7] An important conclusion that can be drawn now is that the traps responsible for the trap-limited current in the purified MEH-PPV are not the same as the (deep) traps that are responsible for the hysteresis. The exponential trap distribution is therefore represented by Q_s in Fig. 2. By now adding a single deep trap level with a concentration N_{td} of 2×10^{16} cm^{-3} with a trap

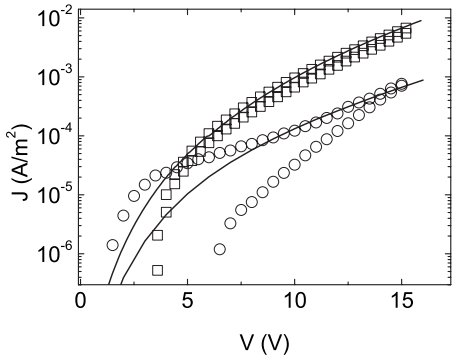

FIG. 8. *J-V* characteristics of an electron-only device of the purified MEH-PPV with L=300 nm (squares) and an electron-only device not purified (circles) together with the calculated currents for an exponential distribution (solid line) and the addition of deep traps (dashed line).

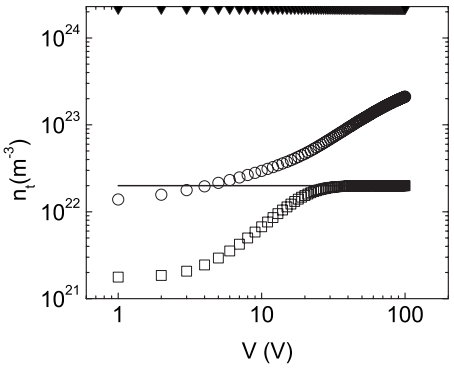

FIG. 9. Density of trapped electrons vs voltage of an unpurified electron-only device with a thickness of 340 nm. The squares represent the density of electrons trapped in the single deep trap level, the circles represent the density of trapped electrons in the shallow traps, characterized by an exponential distribution in energy. The solid line and the triangles represent the total amount of deep and shallow traps in the device, respectively.

depth of ~0.7 eV we can describe the *J-V* characteristics of unpurified MEH-PPV reasonable well, in spite of the simple assumption of only a single trap level. The trap concentration agrees well with the estimation of the amount of trapped charges that stay behind in the device after a *J-V* sweep, as shown in Fig. 3. The deep traps responsible for the hysteresis correspond to Q_d in Fig. 2.

It should be noted that the presence of a single deep trap level is expected to lead to an anomaly in the *J-V* characteristics, the trap-filled limit (TFL). For a deep trap this transition occurs at a voltage V_{TFL} given by[8] $V_{\mathrm{TFL}}=q(N_{td}-n_{td})L^2/2\varepsilon_0\varepsilon_r$ with $(N_{td}-n_{td})$ the concentration of unoccupied deep traps, L the sample thickness, and $\varepsilon_0\varepsilon_r$ the permittivity. Using $(N_{td}-n_{td})-2\times10^{16}$ cm^{-3}, $L=340$ nm, and $\varepsilon_r\sim2.1$ this current anomaly should be expected to set in at $V_{\mathrm{TFL}}=\sim10$ V. The absence of such an anomaly in our experimental *J-V* characteristics seems to contradict the presence of deep traps in our samples. For this reason, we plot in Fig. 9 the numerically calculated densities of deep and shallow trapped electrons versus voltage for an electron-only device of unpurified MEH-PPV with a thickness of 340 nm. It is shown, as expected, that for $V>10$ V the injected charges quickly fill up the deep traps. Since, however, the deep traps in our samples are accompanied by shallow traps that are exponentially distributed in energy, giving rise to a steep *J-V* characteristic[7] of $J\sim V^6$ the TFL transition of the deep traps is masked.

The observation of two types of electron traps corresponds with the earlier observation from thermally stimulated currents: in this study two main charge traps were found after excitation with light, with activation energies of 0.2–0.35 eV and 0.75–0.91 eV, respectively.[12] A possible origin for the deep traps are hydrated oxygen clusters $O_2(H_2O)_n$, which are located at around 3.7 eV below vacuum, leading to a 0.8 eV deep trap for MEH-PPV and MDMO-PPV.[13] However, keeping our samples for 24 h in vacuum (10^{-7} mbar) before deposition of the top-electrode did not lead to any improvement in the hysteresis behavior. Furthermore, the addition of Na_2S0_4 to the polymer solution also did not have any influence on the appearance of the hysteresis, suggesting that oxygen related defects might not be the origin. Another possible origin for the deep traps can be assigned to the presence of carbonyl containing end-groups in the polymer structure. Indeed detailed ^{13}C-NMR studies have shown that Gilch PPV's contain mainly aldehyde and carboxylic acid end-groups.[14] These electron accepting functionalities could be reduced electrochemically via reaction with the injected electrons and thus act as deep traps). Purification leads to fractionation which allows to remove the lower molecular weight polymers and oligomers from the original batch. The resulting high molecular weight fraction will contain a strongly reduced number of said end-groups possibly leading to a decrease in the number of deep traps in the polymer. The effect of the amount of low molecular weight fraction is a subject of further investigations.

IV. CONCLUSION

In conclusion, we demonstrate that the strong hysteresis observed in the electron currents of PPV-based conjugated polymers can be attributed to the presence of deep traps. These traps are persistently occupied after a *J-V* sweep, leading to clockwise hysteresis. The deep traps are not located at the interface between the polymer and the hole-blocking electrode, but are present in the polymer itself. By proper purification of the PPV-based polymers hysteresis free electron currents can be obtained.

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